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APPLICATION NUMBER: *60/545,772*
FILING DATE: *February 19, 2004*
RELATED PCT APPLICATION NUMBER: *PCT/US05/05088*

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

Express Mail Label No.: **EL 993859814 US**

INVENTOR(S)		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Paul	Kohl	Atlanta, GA
Christopher W.	Moore	Atlanta, GA
Jun	Li	Atlanta, GA
Justin	Tullis	Stone Mountain, GA

☐ *Additional Inventors are being named on the separately numbered sheets attached hereto.*

TITLE OF THE INVENTION (500 characters max)

THIN-FILM MEMBRANES FOR FUEL CELLS

CORRESPONDENCE ADDRESS

Direct all correspondence to:

☐ Customer Number: 24504

OR

NAME	Christopher B. Linder, Ph.D. Thomas, Kayden, Horstemeyer & Risley, L.L.P.				
ADDRESS	100 Galleria Parkway Suite 1750				
CITY	Atlanta	STATE	Georgia	ZIP CODE	30339-5948
COUNTRY	U.S.A.	TELEPHONE	770-933-9500	FAX	770-951-0933

ENCLOSED APPLICATION PARTS (*check all that apply*)

☒ Specification *Number of Pages* 25 ☐ CD(s), Number

☐ Drawing(s) *Number of Pages* _____ ☐ Other (Specify)

☐ Application Data Sheet. See 37 CFR 1.76.

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☒ Applicant claims small entity status. See 37 CFR 1.27

☒ A check or money order is enclosed to cover the filing fees

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FILING FEE AMOUNT ($): 80.00

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The PTO did not receive the following listed item(s) Page 21 Total: 24 pages

Respectfully submitted,

SIGNATURE: _____ Date: 2/19/04

TYPE or PRINTED NAME: **Christopher B. Linder, Ph.D.** REGISTRATION NO.: **47,751**

TELEPHONE: (770) 933-9500 DOCKET NO.: **62004-8770**

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 USC 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450 DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Patent Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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FEE TRANSMITTAL for FY 2004

Effective 10/01/2003. Patent fees are subject to annual revisions.

	Complete If Known
Application Number	TBA
Filing Date	February 19, 2004
First Named Inventor	Kohl, et al.
Examiner Name	TBA
Group / Art Unit	TBA
Attorney Docket No.	62004-8770

☒ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 80.00

METHOD OF PAYMENT *(check all that apply)*

☒ Check ☐ Credit Card ☐ Money Order ☐ Other ☐ None

☒ Deposit Account

Deposit Account Number: 20-0778

Deposit Account Name: Thomas, Kayden, Horstemeyer Risley, L.L.P.

The Commissioner is authorized to: *(check all that apply)*

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
1001	770	2001	385	Utility Filing Fee	
1002 *	340	2002	170	Design Filing Fee	
1003	530	2003	265	Plant Filing Fee	
1004	770	2004	385	Reissue Filing Fee	
1005	160	2005	80	Provisional Filing Fee	80.00

SUBTOTAL (1) ($)80.00

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

	Extra Claims			Fee From Below	Fee Paid
Total Claims		- 20** =		X 9.00 =	
Independent Claims		- 3** =		X 43.00 =	
Multiple Dependent				145.00 =	

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
1202	18	2202	9	Claims in excess of 20
1201	86	2201	43	Independent claims in excess of 3
1203	290	2203	145	Multiple dependent claim, if not paid
1204	86	2204	43	**Reissue independent claims over original patent
1205	18	2205	9	**Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($)

**or number previously paid, if greater; For Reissues, see above

FEES CALCULATION *(continued)*

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
1051	130	2051	65	Surcharge-late filing fee or oath	
1052	50	2052	25	Surcharge-late provisional filing fee or cover sheet	
1053	130	1053	130	Non-English specification	
1812	2,520	1812	2,520	For filing a request for *ex parte* reexamination	
1804	920*	1804	920*	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1805	1,840*	Requesting publication of SIR after Examiner action	
1251	110	2251	55	Extension for reply within first month	
1252	420	2252	210	Extension for reply within second month	
1253	950	2253	475	Extension for reply within third month	
1254	1,480	2254	740	Extension for reply within fourth month	
1255	2,010	2255	1,005	Extension for reply within fifth month	
1401	330	2401	165	Notice of Appeal	
1402	330	2402	165	Filing a brief in support of an appeal	
1403	290	2403	145	Request for oral hearing	
1451	1,510	1451	1,510	Petition to institute a public use proceeding	
1452	110	2452	55	Petition to revive-unavoidable	
1453	1,330	2453	655	Petition to revive-unintentional	
1501	1,330	2501	665	Utility issue fee (or reissue)	
1502	480	2502	240	Design issue fee	
1503	640	2503	320	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	50	1807	50	Processing fee for provisional application	
1806	180	1806	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	770	2809	385	Filing a submission after final rejection (37 CFR § 1.129(a))	
1810	770	2810	385	For each add. invention to be examined (37 CFR 1.129(b))	
1801	770	2801	385	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited exam. of a design application	
				Other fee (specify)	

SUBTOTAL (3) ($)

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SUBMITTED BY			Complete (if applicable)	
Typed or Printed Name	Christopher B. Linder, Ph.D.	Registration No. 47,751	Telephone Number	770-933-9500
Signature			Date	2/19/04

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PATENTS
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Kohl, et al.

For: Thin-Film Membranes for Fuel Cells

CERTIFICATE OF EXPRESS MAIL
FOR PROVISIONAL APPLICATION

Mail Stop Provisional Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

Enclosed for filing in the above case are the following documents:

Provisional Application Patent Cover Sheet (1 Page)
Provisional Application Consisting of:
25 Page(s) of Specification
Fee Transmittal Form
Provisional Application Filing Fee - $80.00
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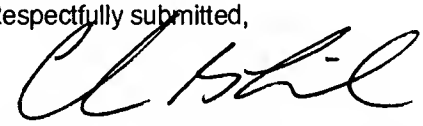
Further, the Commissioner is authorized to charge Deposit Account No. 20-0778 for any additional fees required. The Commissioner is requested to credit any excess fee paid to Deposit Account No. 20-0778.

Respectfully submitted,



Christopher B. Linder, Reg. No. 47,751

THOMAS, KAYDEN, HORSTEMEYER & RISLEY
100 Galleria Parkway, N.W.
Suite 1750
Atlanta, Georgia 30339-5948

Our Reference No: **62004-8770**

I hereby certify that all correspondences listed above are being deposited for delivery to the above addressee, with the United States Postal Service **"EXPRESS MAIL POST OFFICE TO ADDRESSEE"** service under 37 CFR §1.10 on the date indicated below.

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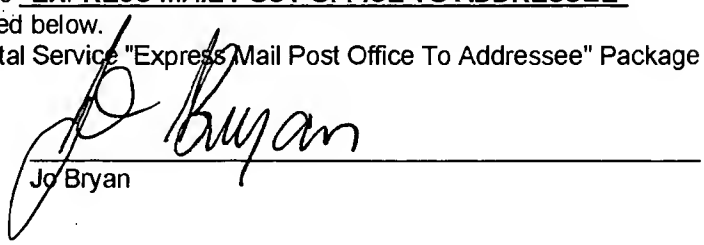
2/9/04
Date



Jo Bryan

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Thin-film Membranes for Fuel Cells
Disclosure Summary

Thin-film membranes for use in proton exchange membrane (PEM) fuel cells have been developed. Also included in the development are ways in which to support these films. These membranes are made through common micro-fabrication techniques, including spin-coating and plasma enhanced chemical vapor deposition (PECVD), and can have a thickness up to 20 micrometers. The materials include polymers, silicon dioxide, and doped silicon dioxide. PEM fuel cells membranes work by conducting protons from the cell anode to cathode. The thinner the membrane, the easier it is for protons to move through it, thus increasing the amount of electrical current that can be generated. Meanwhile, these thin-film materials are superior to currently used PEMs in preventing reactants from passing through the membrane, a common problem particularly in direct methanol fuel cells.

One expected use of these thin-film membranes is in micro fabricated fuel cells. The films would be deposited directly onto the substrate during the fabrication sequence. One example of this is in a previous disclosure for micro fabricated fuel cells where the membrane is deposited onto a patterned sacrificial material, which when removed leaves microchannels for fuel flow.

In other applications, the delicate nature of such a thin material requires that it be supported. The support structures include anything with small holes or porous materials, such as fritted glass or a gas diffusion layer. A filler material, such as wax or polymer, is used to fill in the holes. It is then polished to expose the support structure. The membrane is then deposited on the smooth surface. Removal of the filler material leaves the supported membrane with exposed areas for contact between the membrane and reactants. Alternately, the use of a filler material with a high permeability to the reactants would not require its removal.

The fuel cell catalyst can be deposited with these membranes in a variety of methods, including through inks or sputtering. The deposition can be onto or into the support, in between the filler and membrane, or even imbedded into a non-removed filler.

Figure 1 shows a schematic diagram of a supported membrane in its testing setup. Figures 2 and 3 show the polarization curve for a 3-um thick SiO_2 film deposited onto a gas diffusion layer with a platinum catalyst loading of 0.35 mg/cm^2.

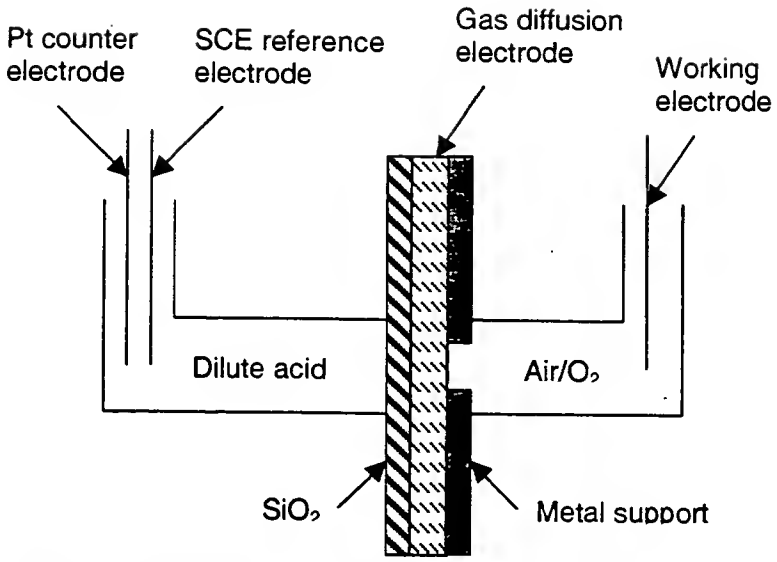


Figure 1: Thin-film membrane support and testing setup

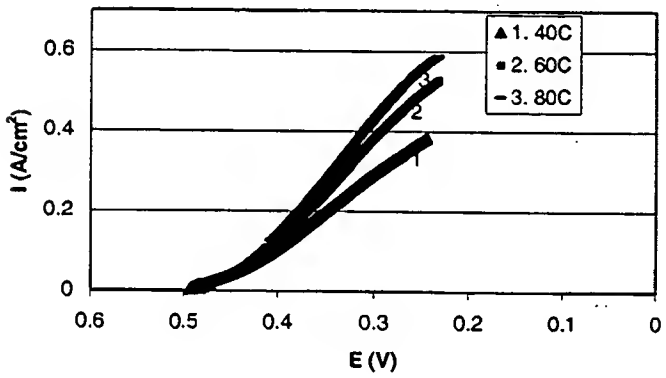


Figure 2: Cathode (air/O_2 half cell) polarization performance

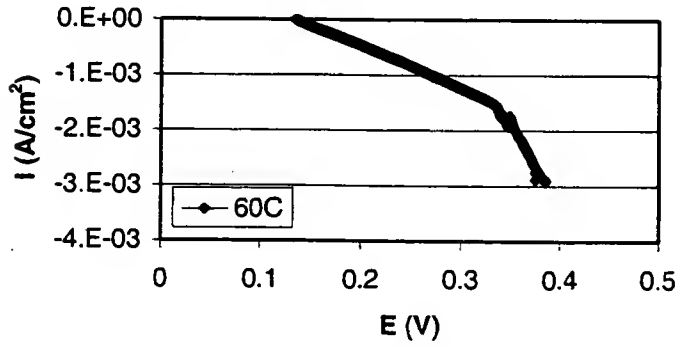


Figure 3: Anode (2M methanol) polarization performance

Thin-film Membranes for Fuel Cells

The following is the first written description of using plasma-deposited SiO_2 membranes in microfabricated fuel cells. The concept has been expanded to include other thin-film materials, including doped SiO_2, and other fuel cell uses.

Plasma-deposited silicon dioxide was used as an overcoat material. The advantage of SiO_2 membranes compared to more traditional materials is the thickness. Table 1.1 below shows a comparison of possible membrane materials for use in thin film fuel cells. Nafion has a higher conductivity, but the films used are much thicker than plasma-deposited SiO_2 layers that can be less than 1 μm. This is important because the resistance (R) of the membrane is related to both its resistivity and thickness. $R = (\rho t)/A$, where ρ is resistivity, t is the thickness, and A is the area. Thus, an important figure of merit for comparing different membranes is the product ρt. While Nafion's resistivity is lower than the low-temperature-deposited SiO_2, the thinner SiO_2 films should give similar resistances.

Table 1: Fuel cell membrane resistances

Material	Resistivity (Ω-cm)	Thickness (μm)	$\rho t = RA$ (Ω-cm^2)
Nafion	100	100	1.0
High temp. SiO_2 (1)	10^6	0.5	50
Low temp. SiO_2	10,000	0.5	0.5

Thin-Film Membrane Materials for Use in Microfabricated Direct Methanol Fuel Cells

Christopher Moore, Jun Li, and Paul Kohl

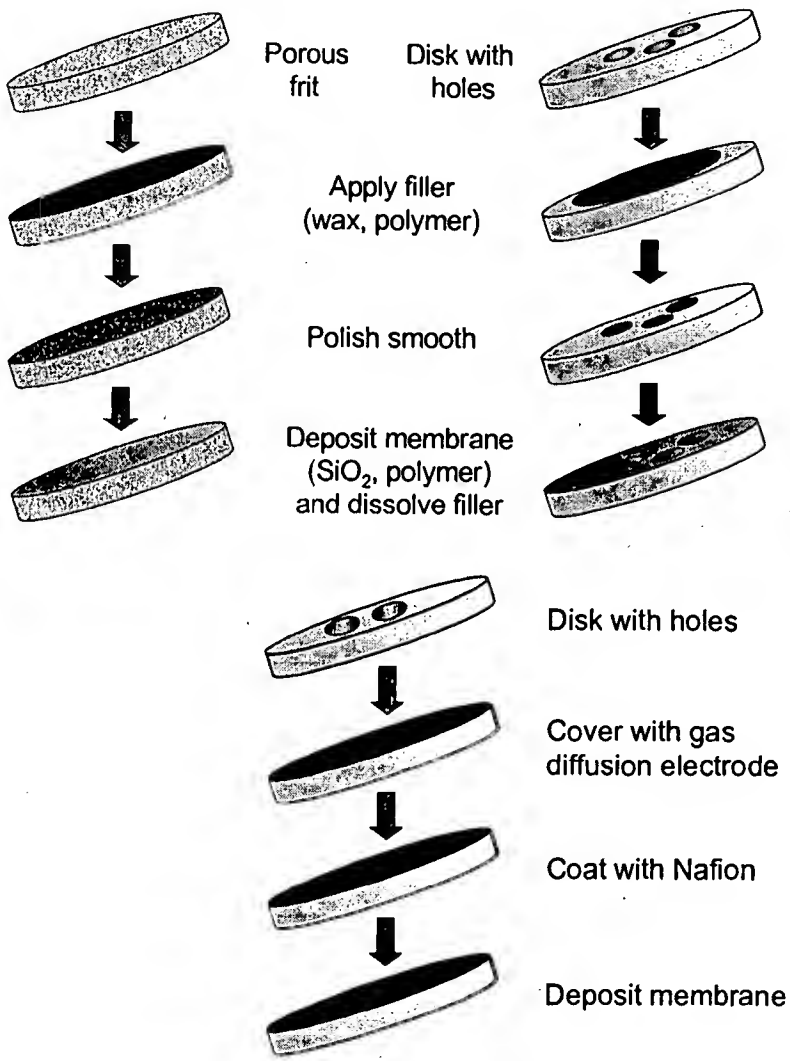
Georgia Institute of Technology

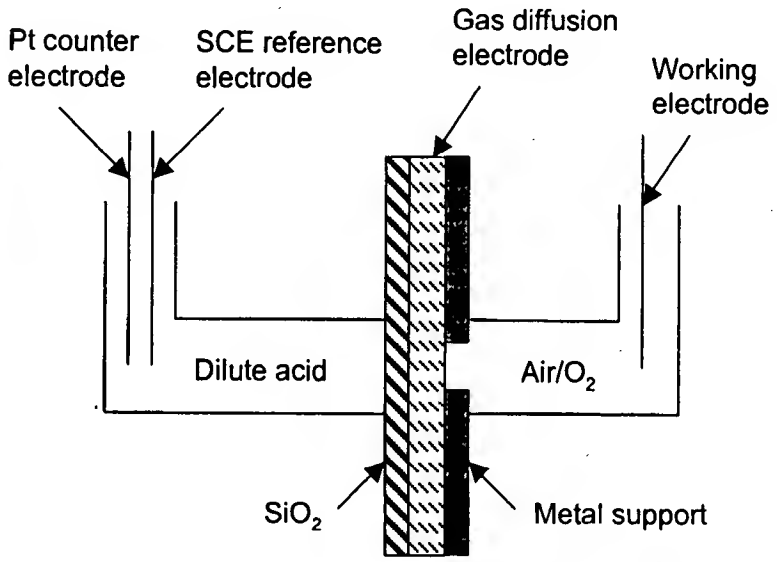
School of Chemical and Bimolecular Engineering

Introduction

- Motivation
  - Fuel cells offer higher energy density power sources for portable electronics
  - Methanol is conveniently stored in liquid form
  - Improvements must be made to reduce methanol crossover for more concentrated fuel
- Current Work
  - Microfabricated direct methanol fuel cells
  - Integrated on silicon wafer with integrated circuits
- Desired Characteristics of Membranes
  - Thickness: 0.1 – 10 μm
  - Conductivity: 0.01 S/cm
  - Extremely low methanol crossover
  - Good performance at low relative humidity

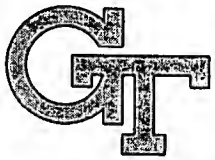
Membrane Support and Testing





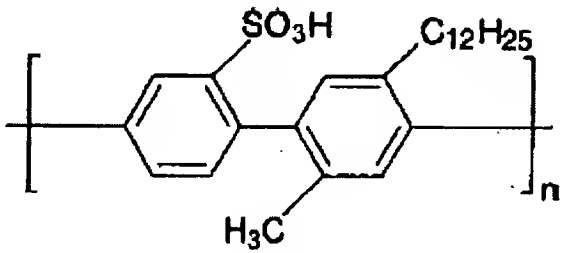
Catalytic Electrodes

- Porous layer of sputtered platinum-ruthenium at both the anode and the cathode
  - Contact between reactants, catalyst, and membrane
  - Enough platinum to be electrically conductive
- Advantages
  - Lower Pt loading
    - O'Hayre, et al. J. Power Sources **109** (2002) 483-493
  - Reduction of methanol crossover
    - Choi, et al. J. Power Sources **96** (2001) 411-414



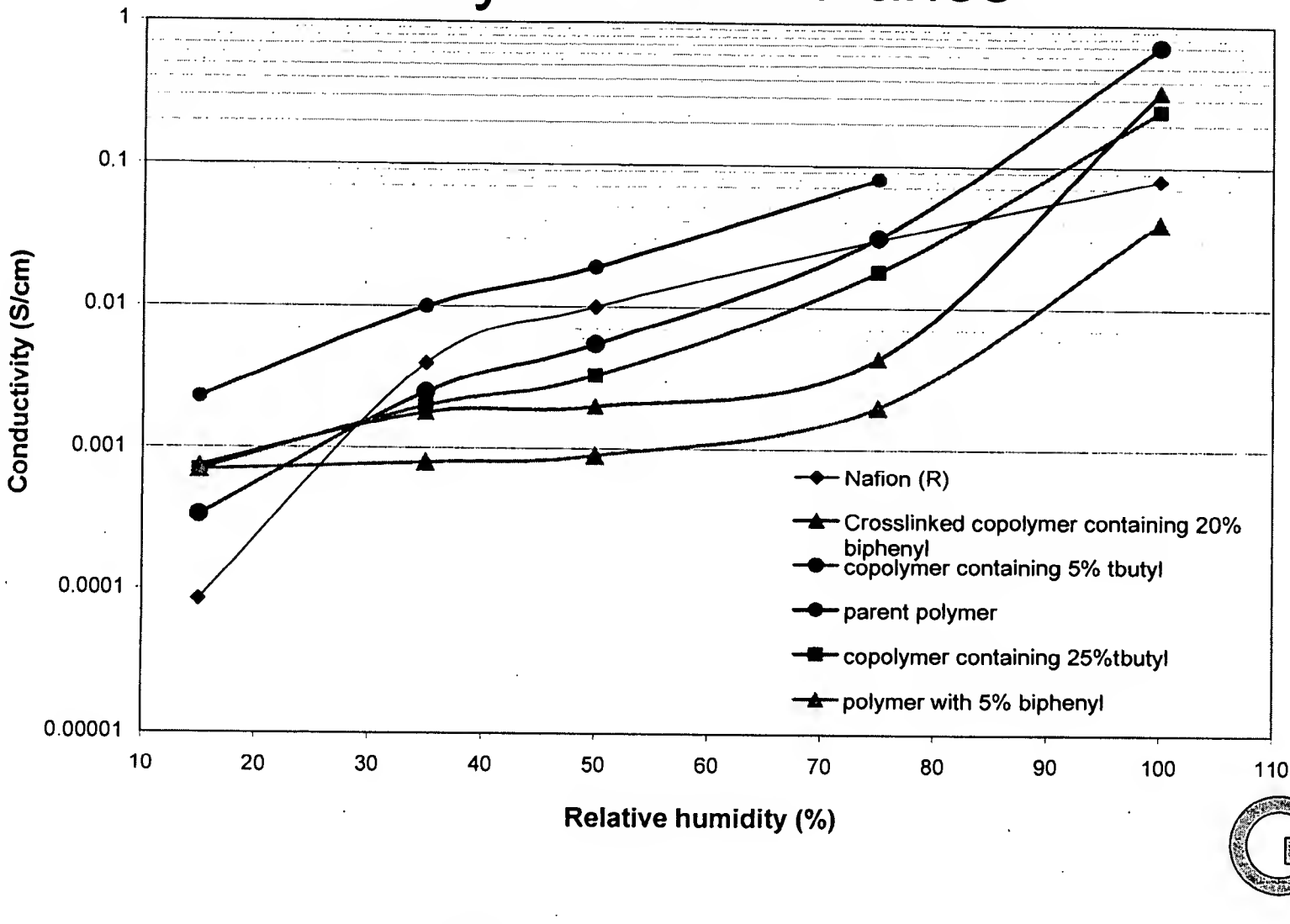
Polyphenylene Sulfonic Acid

- Received from Case Western Reserve University
  - Dr. Morton Litt and Sergio Granados-Focil



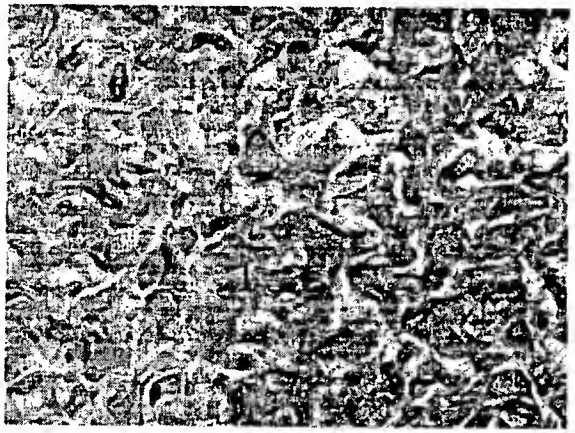
- Soluble in water and methanol
- Needs to be crosslinked for mechanical stability

Proton Conductivity of Water Insoluble Polymer Membranes

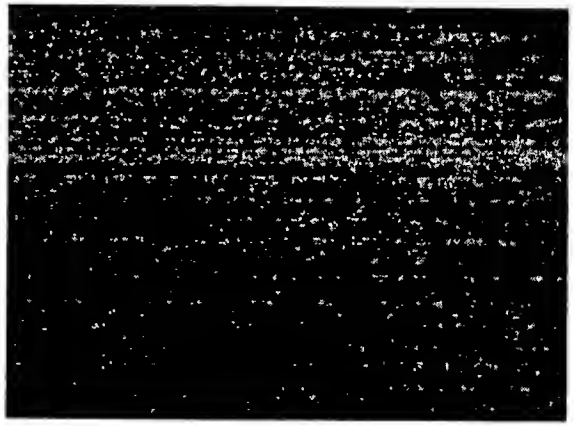


Polyphenylene Sulfonic Acid Crosslinking

- PPSA films spin coated to thickness of 1 μm
- Electron beam exposure at 100°C
- No significant change in PPSA thickness
- PPSA film no longer soluble in water or methanol

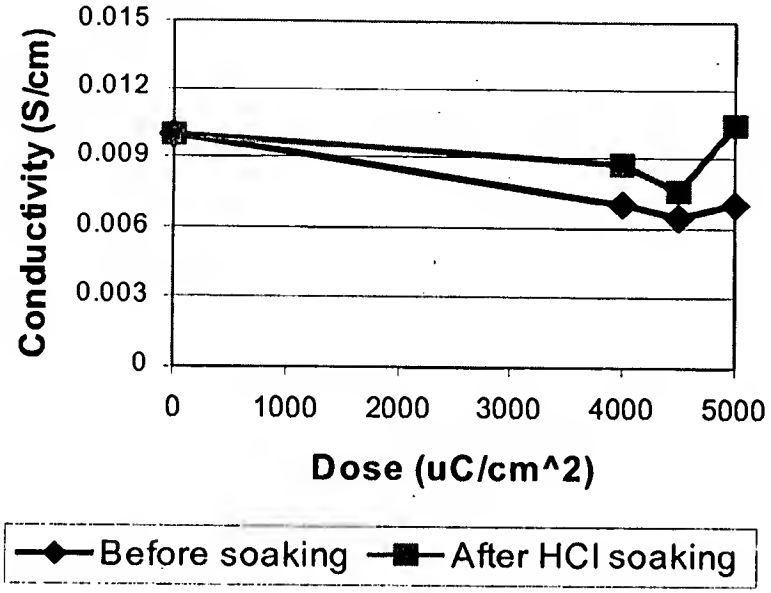


Before crosslinking



After crosslinking

Conductivity of PPSA



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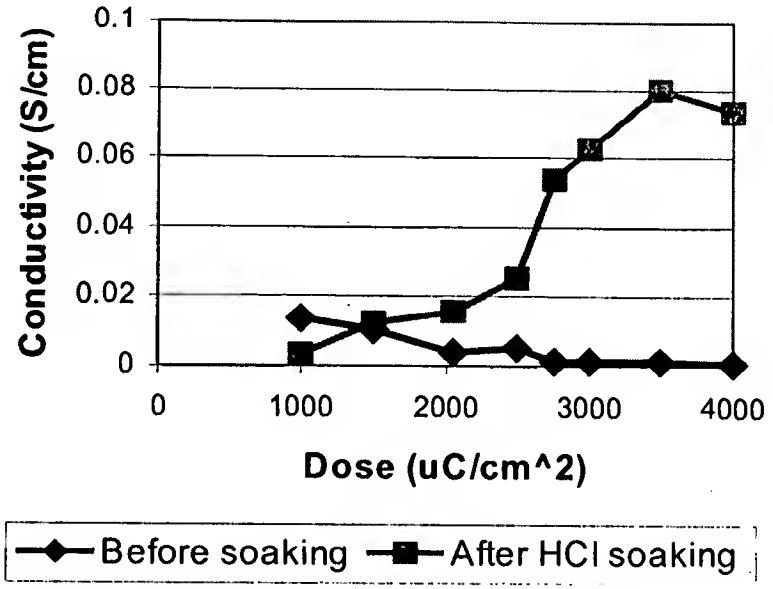


Doped with Diazide

- Soaked in 10% HCl for 24 hours
  - Increased ionic conductivity
- 3 wt% diazide* added to PPSA
  - Promotes crosslinking, thus reducing necessary electron beam dose

*2, 6-bis(4-azidobenzylidene)-4-ethyl cyclohexanone

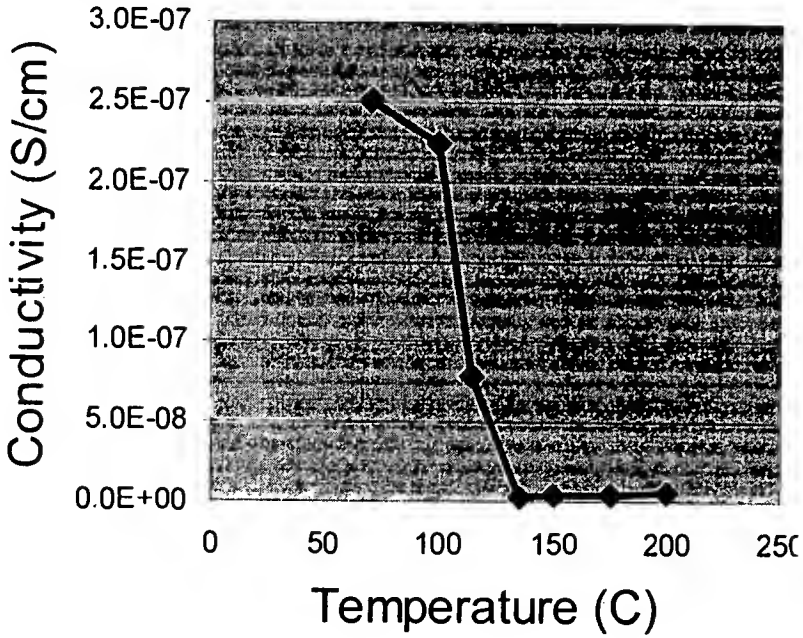
Silicon Dioxide as a Membrane

- Plasma-Enhanced Chemical Vapor Deposition (PECVD) at 75-150°C
  - Temperature is shown to have a large effect on permittivity and loss*
    - Lower temperatures lead to increased silanol and water concentrations
    - The hydroxyl groups lead to increased polarity, and therefore higher ionic conductivity
- Support for polymer membranes
  - Mechanical support
  - Solvent Barrier
- Possible stand-alone membrane

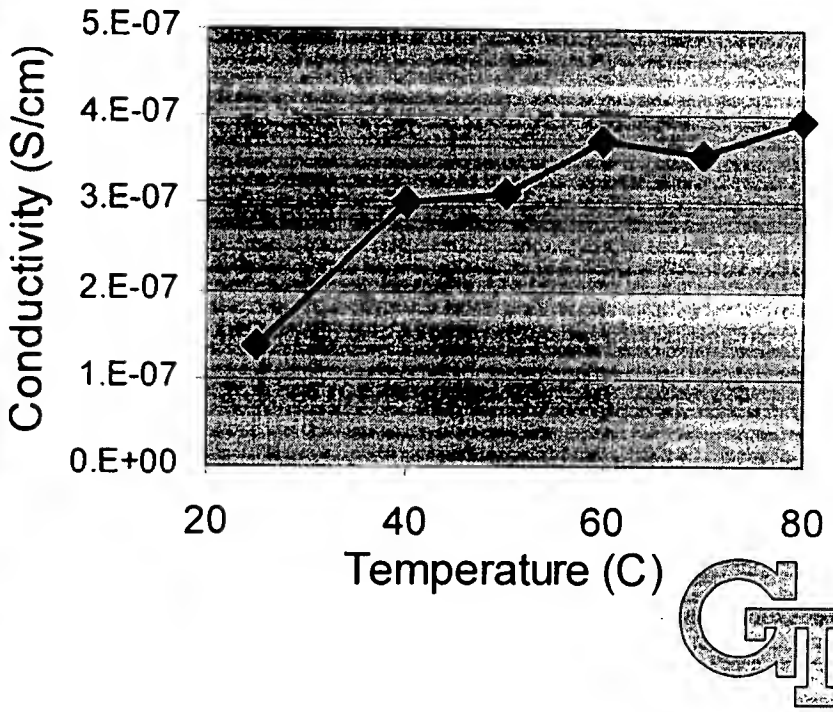
* Ceiler, Kohl, and Bidstrup, *J. Electrochemical Society*, Vol. 142, No. 6, pp. 2067-2071

Conductivity of Silicon Dioxide

- Increasing ionic conductivity of SiO_2 films with decreasing deposition temperature
- Measured through the use of impedance spectroscopy



- Increasing ionic conductivity of SiO_2 films with increase in temperature
- Measured through current step experiments



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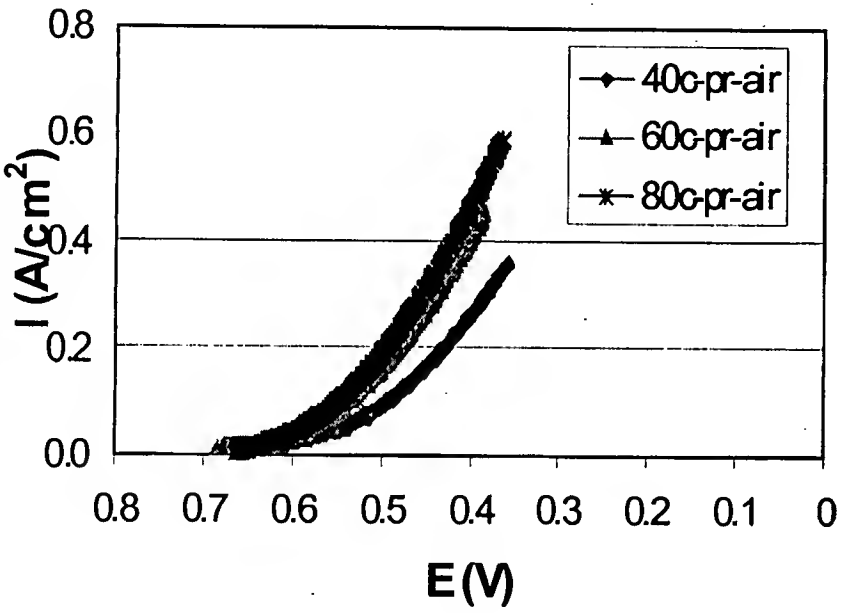
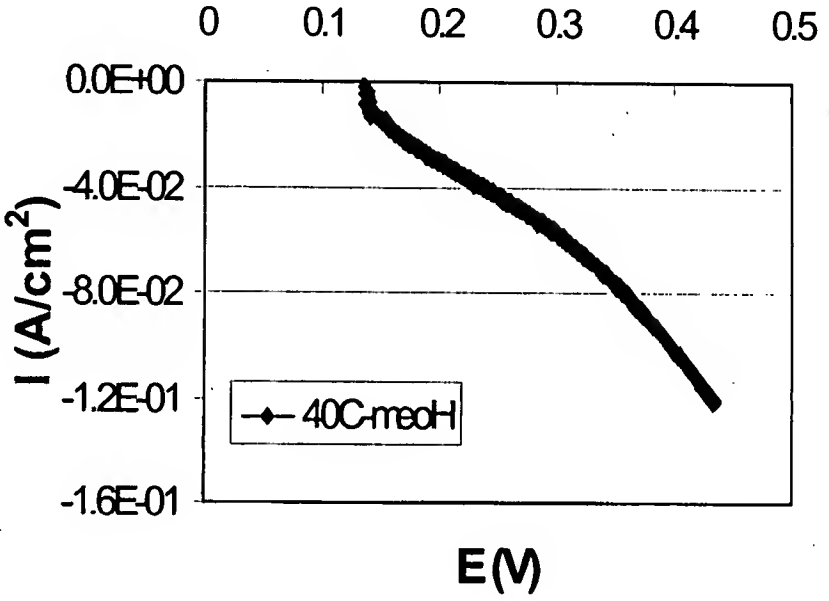
SiO_2 Membrane Performance

Pressurized Air Reduction



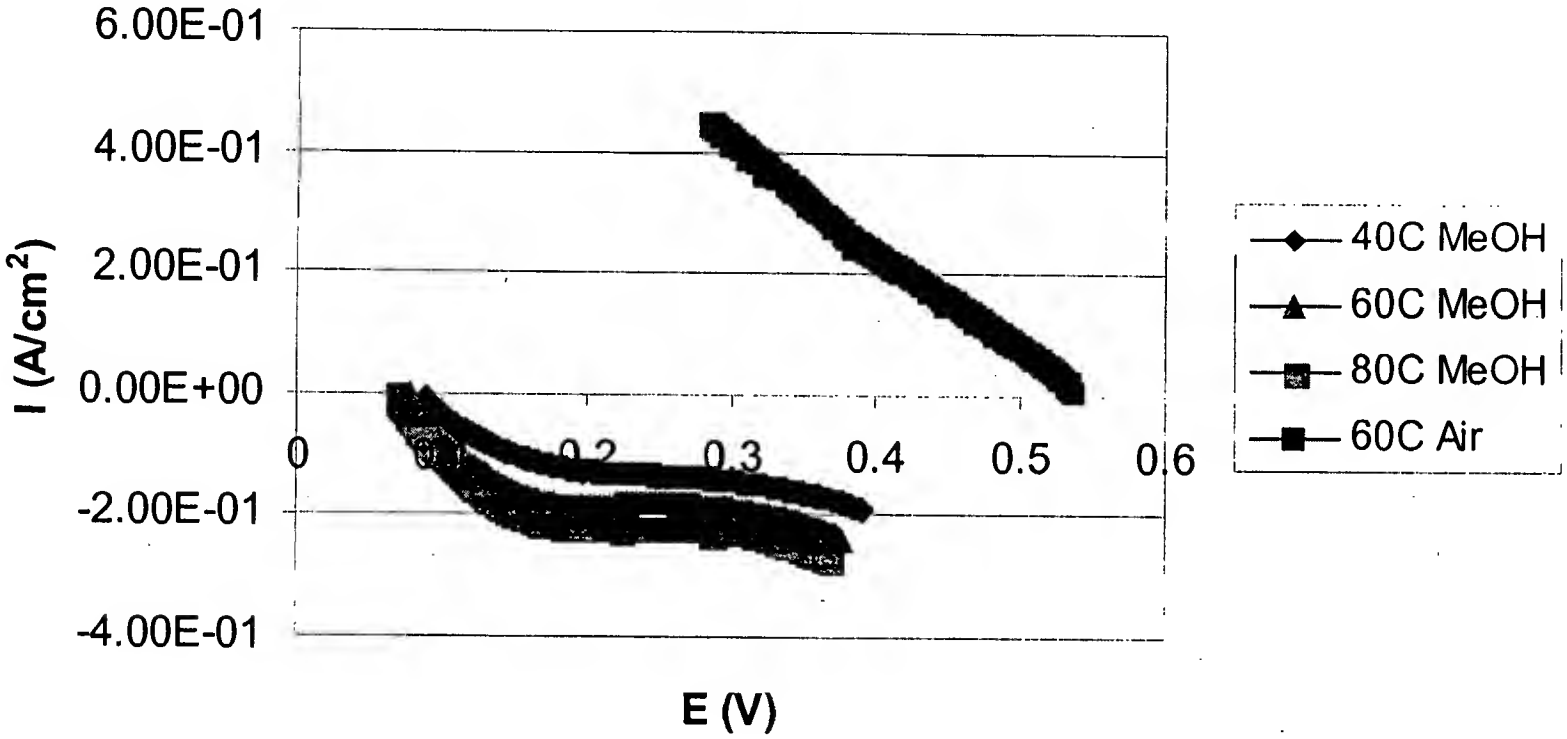
Methanol Oxidation



14

SiO_2 thickness = 3.0 um
Preloaded Pt catalyst
Voltage vs. SCE
Scan rate = 1 mV/s

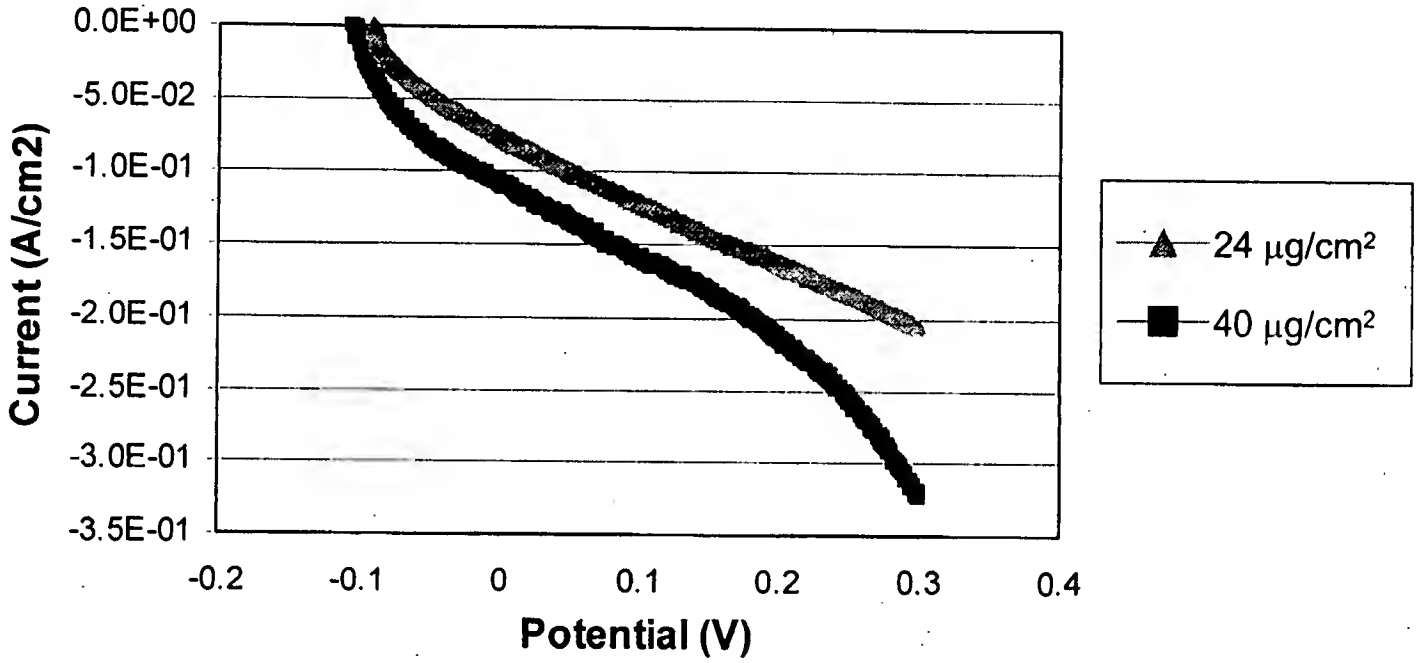
SiO_2 Membrane Performance



SiO_2 thickness = 1.8 um
Preloaded Pt-Ru catalyst
Voltage vs. SCE
Scan rate = 1 mV/s

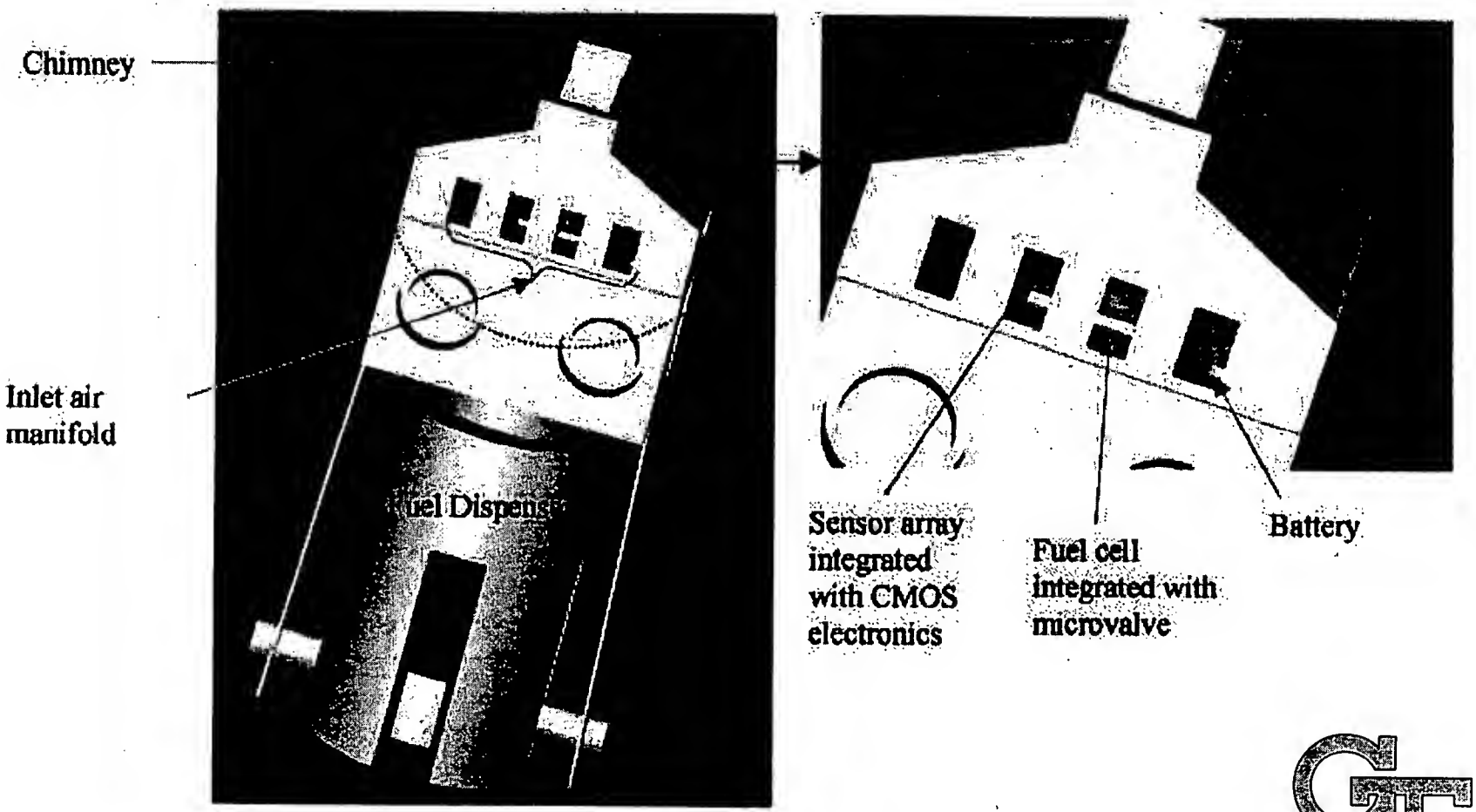
15

Sputtered Catalyst Performance

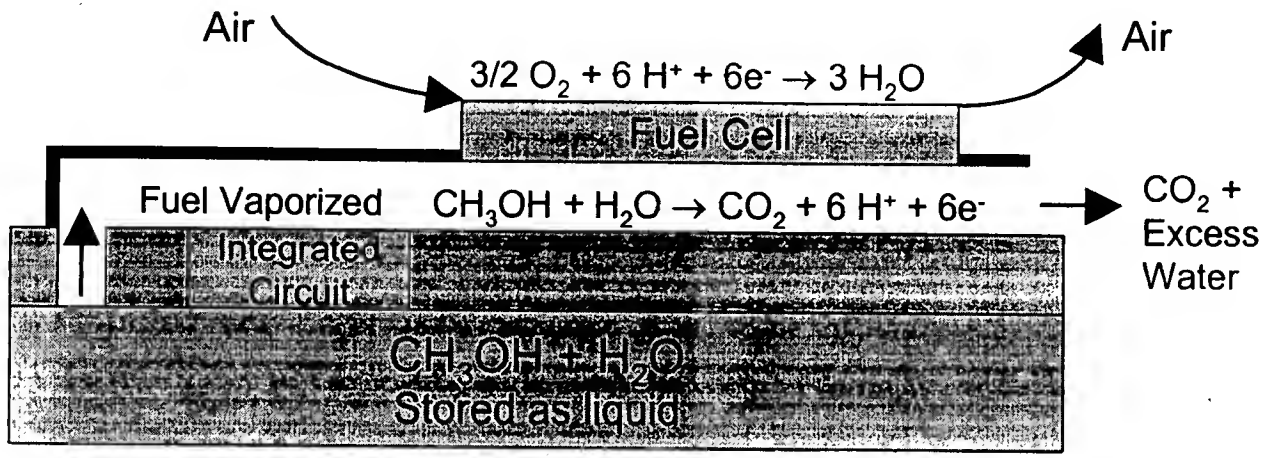


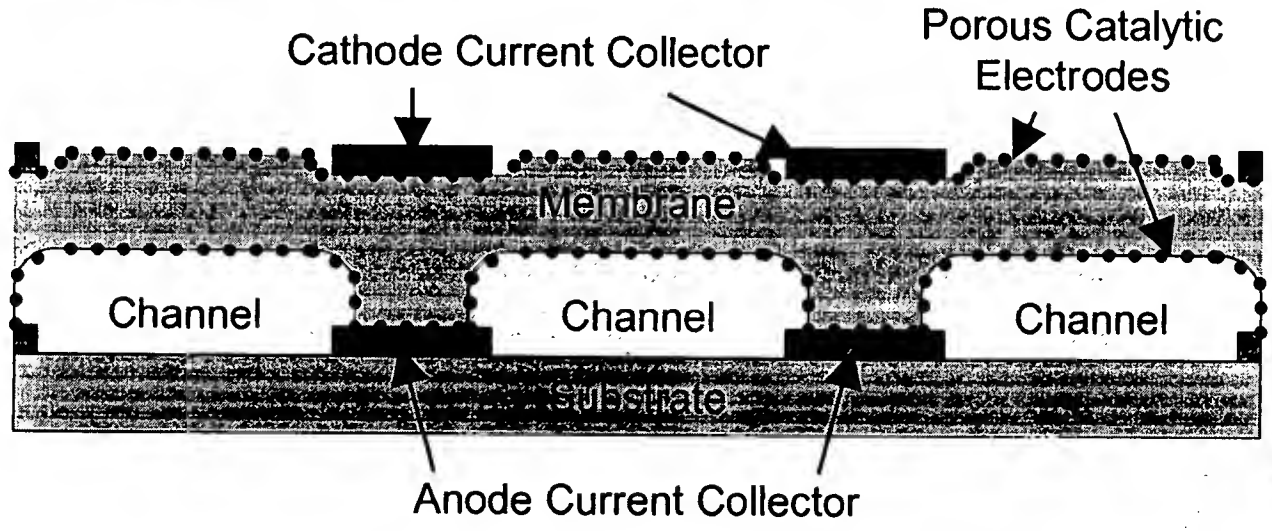
Temperature = 60°C
SiO_2 thickness = 3.2 um
Sputtered Pt-Ru catalyst
Voltage vs. SCE
Scan rate = 1 mV/s

Integrated Micro Fuel Cell/Si CMOS/Sensor Technology

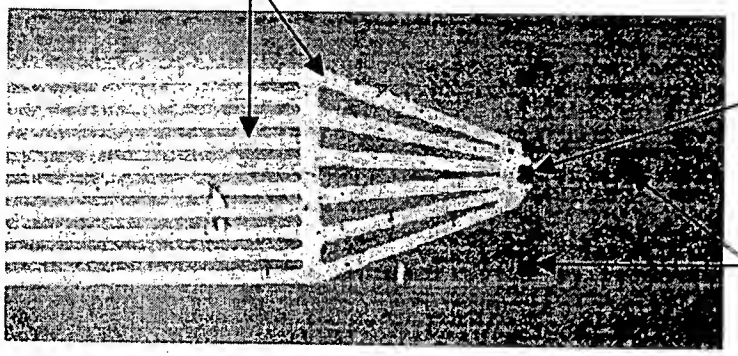


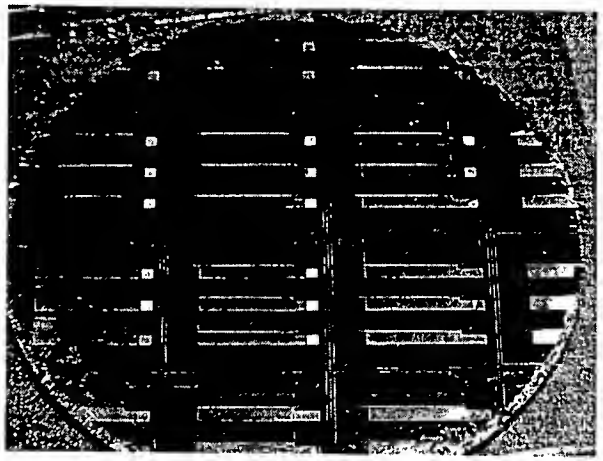
Schematics of Micro Fuel Cell

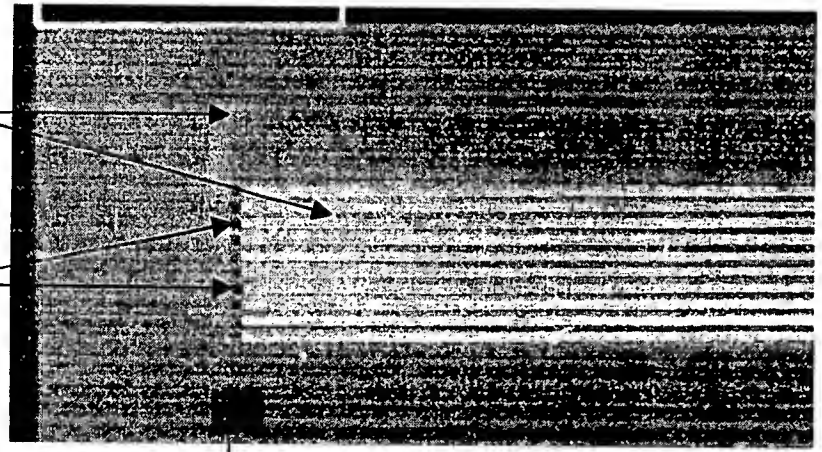


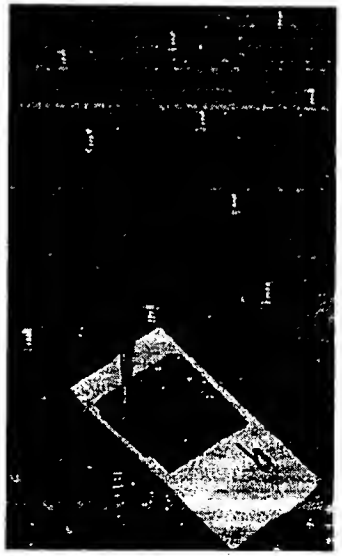


Fabricated Prototypes









Summary

- Thin-film membranes for use in proton exchange membrane (PEM) fuel cells have been developed.
  - Deposited through common microelectronic fabrication techniques, including spin-coating and PECVD
  - Incorporated into microfabricated fuel cell design
  - Needs mechanical support for larger designs
  - Low current density due to low catalyst loading

Thin-film Membranes for Fuel Cells
Disclosure Summary

Thin-film membranes for use in proton exchange membrane (PEM) fuel cells have been developed. Also included in the development are ways in which to support these films. These membranes are made through common micro-fabrication techniques, including spin-coating and plasma enhanced chemical vapor deposition (PECVD), and can have a thickness up to 20 micrometers. The materials include polymers, silicon dioxide, and doped silicon dioxide. The silicon dioxide membrane was deposited so as to have high ionic conductivity for proton exchange. The conditions for ionic conductivity were to have the deposition temperature low, such as 60°C to 200°C. PEM fuel cells membranes work by conducting protons from the cell anode to cathode. The thinner the membrane, the easier it is for protons to move through it, thus increasing the amount of electrical current that can be generated. Meanwhile, these thin-film materials are superior to currently used PEMs in preventing reactants from passing through the membrane, a common problem particularly in direct methanol fuel cells.

Slides 6 and 8 [illegible] shows electron beam crosslinking of a polymer proton exchange membrane. This is the first demonstration of the electron beam crosslinking.

One expected use of these thin-film membranes is in micro fabricated fuel cells. The films would be deposited directly onto the substrate during the fabrication sequence. One example of this is in a previous disclosure for micro fabricated fuel cells where the membrane is deposited onto a patterned sacrificial material, which when removed leaves microchannels for fuel flow.

In other applications, the delicate nature of such a thin material requires that it be supported. The support structures include anything with small holes or porous materials, such as fritted glass or a gas diffusion layer. A filler material, such as wax or polymer, is used to fill in the holes. It is then polished to expose the support structure. The membrane is then deposited on the smooth surface. Removal of the filler material leaves the supported membrane with exposed areas for contact between the membrane and reactants. Alternately, the use of a filler material with a high permeability to the reactants would not require its removal.

The fuel cell catalyst can be deposited with these membranes in a variety of methods, including through inks or sputtering. The deposition can be onto or into the support, in between the filler and membrane, or even imbedded into a non-removed filler.

Figure 1 shows a schematic diagram of a supported membrane in its testing setup. Figures 2 and 3 show the polarization curve for a 3-um thick SiO_2 film deposited onto a gas diffusion layer with a platinum catalyst loading of 0.35 mg/cm^2.

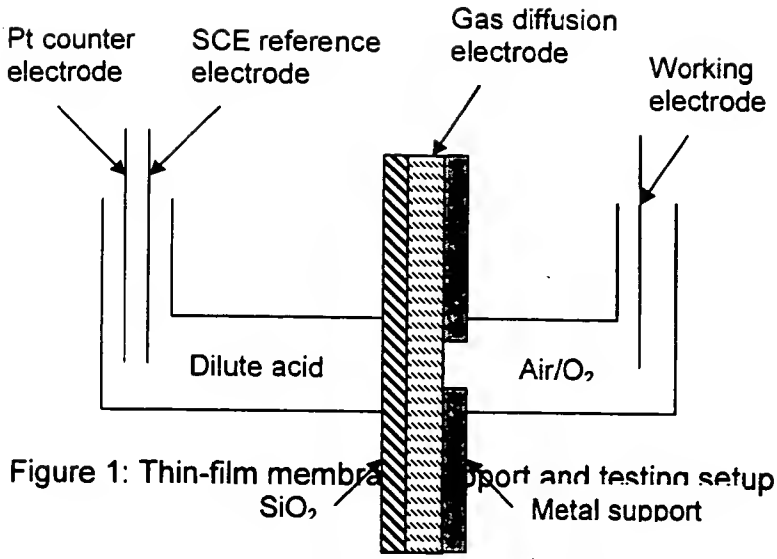


Figure 1: Thin-film membra[illegible]pport and testing setup

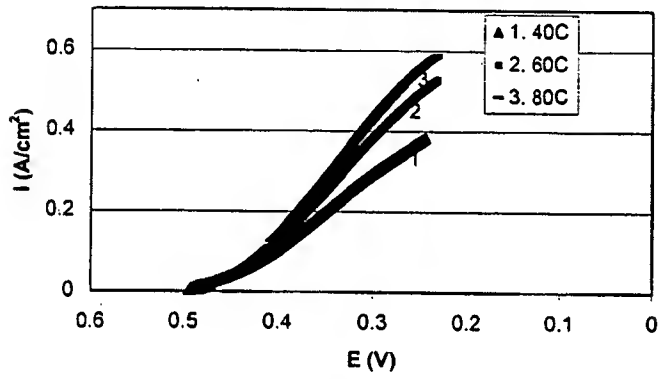


Figure 2: Cathode (air/O_2 half cell) polarization performance

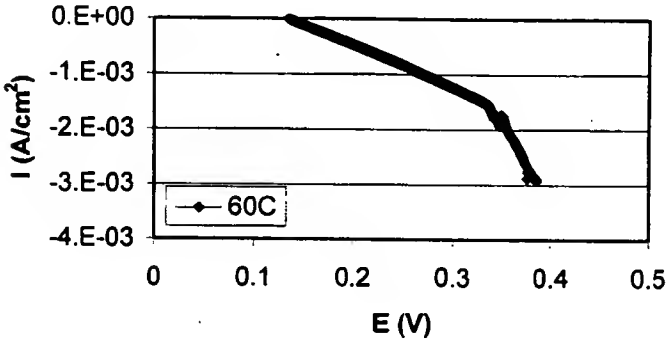


Figure 3: Anode (2M methanol) polarization performance

Design Considerations

The following characteristics are desired for thin-film membranes and membrane-electrode assemblies.

Maximum exposure of membrane to fuel
Maximum activity of catalyst with low loading
High proton conductivity of membrane with no electrical conductivity
High electrical conductivity of current collector
Minimum methanol crossover through membrane, even with high concentrations of methanol feed

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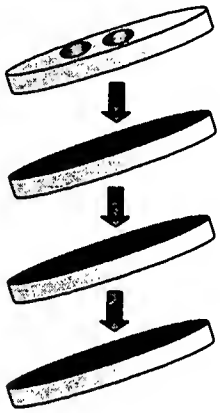
Step-by-Step Fabrication

To fabricate and support a thin-film membrane on a catalytic gas diffusion layer:



Solid support structure with small holes for fuel/membrane contact. A mesh or porous structure may also be used.

Cover the support with the gas diffusion layer (GDL).

If needed, the GDL can be coated with Nafion, or similar material, to fill in any uneven spaces.

Deposit thin film membrane through spin-coating or plasma enhanced chemical vapor deposition.

A process sequence for integrated micro fuel cells:

Fabricate Sensor and CMOS Devices

Overcoat Microchannels with Polymer Electrolyte Membrane

Pattern Sacrificial Polymer for Microchannels

Dielectric Cure and Decomposition of Sacrificial Polymer

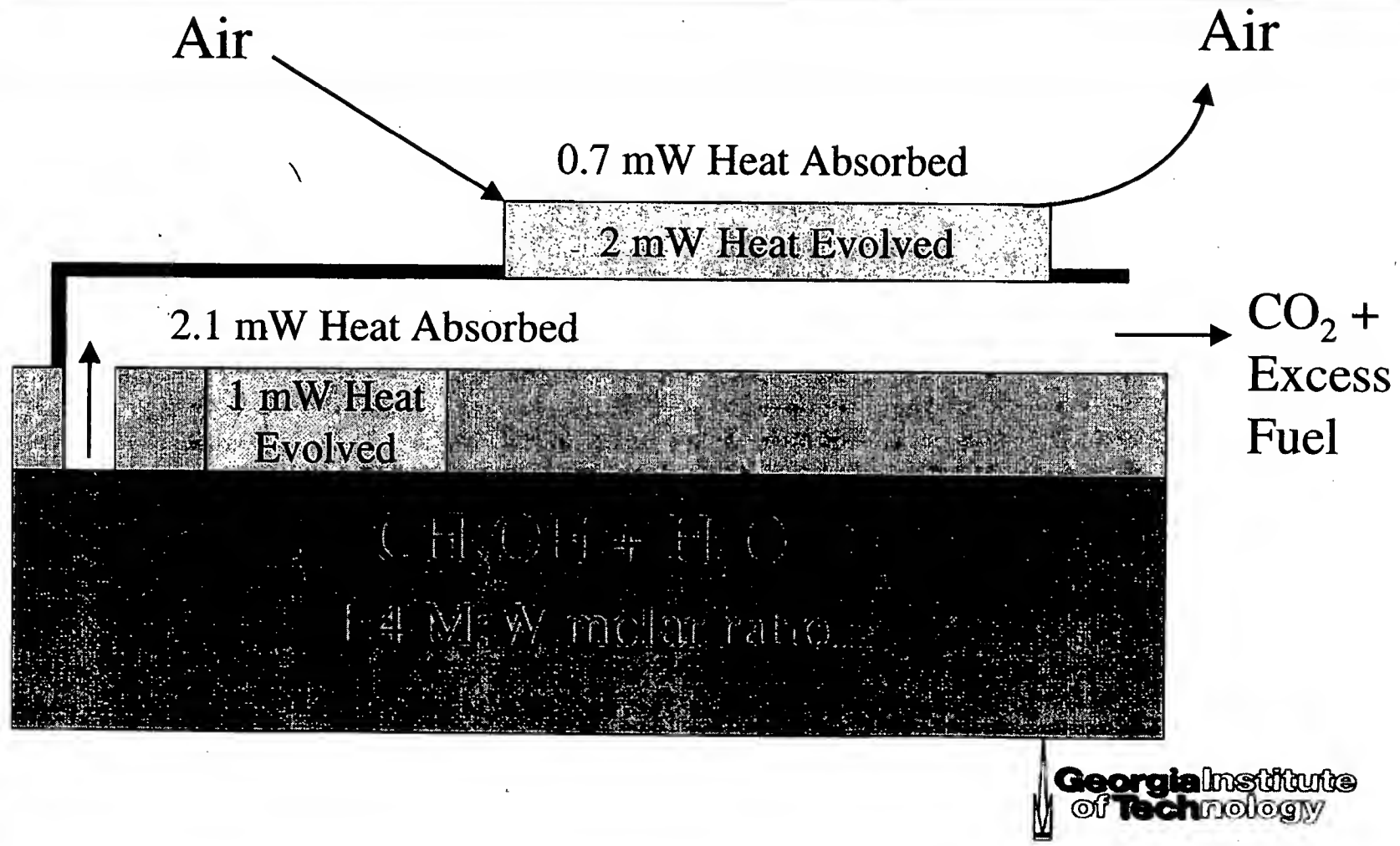
First Metallization of CMOS and Anode Catalyst

Second Metallization of CMOS and Cathode Catalyst

Micro-Fuel Cell

1 mW power at 0.4 V

50% efficiency, No crossover



Georgia Institute of Technology